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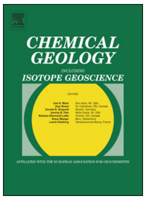

Surface area effects on the reduction of U^{VI} in the presence of synthetic montmorillonite☆

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ABSTRACT

The redox transformations that affect the environmental mobility of metal or radionuclide contaminants typically take place in the presence of mineral or biological surfaces. Adsorption can alter the speciation and free energy of a dissolved ion and can thus change the occurrence, rate, or products of redox reactions relative to those expected in homogenous solution. Here, we investigated the effect of SYn-1, a redox-inactive synthetic montomorillonite clay mineral, on the reduction of U^{VI} by dihydroanthraquinone-2,6 disulfonate (AH_2QDS, the reduced form of the soluble electron shuttle AQDS). We varied the surface:U ratio in a circumneutral bicarbonate solution and measured the valence and atomic coordination of U in the solids using X-ray absorption spectroscopy (XANES and EXAFS). The spectra show that U^{IV} was the predominant product both in the presence or absence of the clay mineral, indicating that adsorption of U^{VI} to clay mineral surface sites does not affect its ability to be reduced by AH_2QDS. In the absence of the clay mineral and at low-to-intermediate surface:U ratios the predominant U^{IV} product was nanoparticulate uraninite, UO_2. At the highest surface:U ratio tested (100 g/L clay mineral and 50 μM U) we observe a decrease in the proportion of uraninite down to 50%, with the remaining U^{IV} present as adsorbed, non-uraninite species. These results are similar to previous findings with magnetite and rutile, where adsorbed U^{IV} were the predominant species below a specific surface coverage and U in excess of this coverage was precipitated as uraninite. The threshold coverage determined here for the SYn-1 clay mineral is 10-100× lower than that determined for magnetite and rutile, suggesting that clay mineral surfaces may be less important than metal oxides for stabilizing non-uraninite U^{IV} species in natural sediments.

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1. Introduction

Uranium (U) is a contaminant of worldwide concern due to the accumulation of waste from its mining and enrichment, as well as due to its continued use for power generation and the resulting on-site storage of spent nuclear fuel (Macfarlane, 2011). U release can result from accidents (e.g., at the Fukushima or the Chernobyl energy plants) (Abe et al., 2014; Salbu et al., 1994), as well as through slow discharge from failing waste containment or from weathering of mine tailings (Meinrath et al., 2003; Riley and Zachara, 1992; Salbu et al., 1994; US-GOA, 2014). Once in the environment, the dispersal of U is controlled by its aqueous interactions with minerals, bacteria, and groundwater constituents, which can include dissolution, complexation, adsorption, redox, mineral precipitation, or mineral incorporation reactions. To predict U transport it is necessary to know the reactants and products, as well as the thermodynamics and kinetics of the major reactions. Presently, however, these reactions are insufficiently characterized and reactive transport models are unable to capture some of the relevant processes necessary to accurately predict the transport and fate of U in the subsurface (Li et al., 2009; Yeh et al., 2013).

Redox reactions are an important reaction subset governing U propagation in subsurface and near-surface environments, where U can encounter naturally-occurring or induced reducing conditions. The potential change in U valence can cause a dramatic change in U solubility and mobility, whereby reduction of U^{VI} (the stable valence in oxygenated groundwater) to U^{IV} can result in the precipitation of the mineral uraninite, UO_{2+x}, which is orders of magnitude less soluble than U^{VI} minerals (Ulrich et al., 2008). Previous studies have shown that respiring bacteria or reduced minerals and dissolved components typically present in subsurface environments are capable of reducing

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U^{VI} to U^{IV} resulting in the formation of uraninite (Hyun et al., 2012; O'Loughlin et al., 2011; Suzuki et al., 2002; Wall and Krumholz, 2006). It has, however, now become well established by spectroscopic measurements that U^{IV} produced in the complex milieu of real sediments often does not precipitate as uraninite on the time scale of months to years (Bargar et al., 2013; Kelly et al., 2008; Kelly et al., 2010; Morin et al., 2016; Sharp et al., 2011). These predominant "non-uraninite" or "monomeric" U^{IV} species are deemed more labile to dissolution than uraninite (Alessi et al., 2012) and are thus expected to control U mobility in the subsurface on timescales relevant to rain events, seasonal changes, and oxic-anoxic fluctuations in wetlands, rivers, or hyporheic zones.

Our understanding of the factors leading to non-uraninite U^{IV} species and their molecular structure (i.e., the reactive species identity) is still very limited. Laboratory studies indicate that phosphate groups can complex U^{IV} and inhibit uraninite formation (Boyanov et al., 2011; Rui et al., 2013; Veeramani et al., 2011), a factor of great importance in systems with biological activity. Bacterial strain and physiology also appear to have an effect on the nature of U^{IV} produced during respiration of U^{VI}, most likely due to alterations of the chemical conditions at the location of electron transfer (Boyanov et al., 2011). Because subsurface environments may or may not have biological components and significant phosphate content, but typically have high mineral:U ratios, the role of minerals in complexing U^{IV} may be significant. Indeed, the ability of metal oxide surfaces (TiO_2 and Fe_3O_4) to complex U^{IV} and prevent uraninite formation over the months-to-years timescale has been recently demonstrated (Latta et al., 2014) and the corresponding U^{IV} adsorption reactions have been quantified (Wang et al., 2015). Clay minerals are another ubiquitous mineral component of soils and sediments that also have important technological applications in nuclear waste barriers (Bergaya and Lagaly, 2013; Dohrmann et al., 2013). The role of clay mineral surface sites in complexing and stabilizing non-uraninite U^{IV} species, however, has not been evaluated.

Here, we examine the effect of an iron-free montmorillonite clay mineral on the U^{IV} species produced by reduction of U^{VI}, as determined by experiments in batch reactors with increasing solids loading. Montmorillonites are dioctahedral alumino-silicates that are present in the clay fraction of soils and rocks (Guven, 1988). In addition to providing binding sites, clay minerals can contain significant amounts of Fe and can have a role in redox reactions (Stucki, 1988). To isolate the effect of surface complexation on U^{IV} speciation from the potential effects of the rate or mechanism of electron transfer from Fe^{II} to U^{VI}, we used an iron-free synthetic montmorillonite known as SYn-1. SYn-1 has a structure similar to reference montmorillonite clay minerals containing Fe (e.g., SWy-2 or NAu-1, which have ~3% and ~30% Fe content, respectively), but has no redox reactivity and <0.02% *w*/w Fe content (Neumann et al., 2013). Reduction of U^{VI} in the SYn-1 reactors was achieved by addition of dihydroanthraquinone-2,6 disulfonate, AH_2QDS (the reduced form of 9,10-anthraquinone-2,6-disulfonic acid, or AQDS), which is a soluble electron shuttle used in studying extracellular electron transfer in bacterial systems (O'Loughlin, 2008) and known from previous work to reduce U^{VI} to nanoparticulate uraninite in the absence of surfaces (Latta et al., 2016). Aqueous U concentrations were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) and the speciation of U in the solids was determined by synchrotron x-ray absorption spectroscopy. The results provide a framework for evaluating the importance of clay minerals relative to that of metal oxides or biological factors in the stabilization of non-uraninite U^{IV} species.

2. Experimental

2.1. Clay mineral preparation

The clay mineral SYn-1 was purchased from the Source Clays Repository of The Clay Mineral Society (www.clays.org). SYn-1 is classified as a synthetic mica-montmorillonite with a chemical formula of $Na_{0.024}(Al_{4.44}Mg_{0.04}Fe_{tr})(Si_{6.5}Al_{1.5})O_{20}(OH)_4$ (Alba et al., 2005; Chipera and Bish, 2001; Mermut and Cano, 2001; Mermut and Lagaly, 2001). The SYn-1 clay mineral was Na^+ homoionized, purified, and size-fractionated to <0.5 μm using the procedures described in (Neumann et al., 2013). The processed particles were confirmed to be free of impurities (boehmite is present as an impurity in raw SYn-1) using FT-IR spectroscopy and X-ray diffraction.

2.2. Reactor setup

All experiments and sample manipulations were conducted under anoxic conditions inside an O_2-free glovebox (<1 ppm O_2 at all times maintained in a 7% H_2/93% N_2 atmosphere using a Pd-catalyst). Oxygen-free solutions were prepared by bubbling 18 MΩ deionized (DI) water with nitrogen gas for 2 h and allowing the N_2-degassed water to stand several days open to the glovebox atmosphere to remove traces of O_2. All buffers and solutions were prepared from de-oxygenated DI water inside the anoxic glovebox.

A solution containing 30 mM 9,10-anthraquinone-2,6-disulfonic acid disodium salt (AQDS, Sigma-Aldrich) was reduced with hydrogen gas over Pd-coated (0.5 wt% Pd) 3.2 mm alumina pellets (Sigma-Aldrich) (Tratnyek and Macalady, 1989). Hydrogen gas was bubbled through the AQDS solution for ~8 h. Complete reduction of the AQDS to the di-hydroquinone form (AH_2QDS) was confirmed by quantitative reduction of a ferric citrate solution to Fe(II) determined by the 1,10-phenanthroline method (Tamura et al., 1974).

The compositions of the reactors used to investigate U^{VI} sorption to SYn-1 and its reduction by AH_2QDS are given in Table 1. A buffer solution of 20 mM 3-(N-Morpholino) propanesulfonic acid (MOPS) containing 20 mM NaCl electrolyte and 2 mM $NaHCO_3$ was used to hold a pH value of 7.2. U^{VI} was added from a stock of 0.1 M uranyl acetate dissolved in 0.1 M HCl. After U^{VI} addition the pH of the reactor was re-adjusted to a value of 7.2 by addition of 1 M NaOH. The clay mineral solids were added to the corresponding volume of solution containing buffer, U^{VI}, and bicarbonate, and dispersed using a probe sonicator inside the anoxic chamber. To minimize the amount of SYn-1 used over the large solids loading range (2 to 100 g/L SYn-1), the reactor volume was varied from 25 mL for 2 g/L SYn-1 reactors to 5 mL for 100 g/L reactors. After a 2 h sorption period, an aliquot of filtered 30 mM AH_2QDS adjusted to a pH of 7.2 was added to achieve the nominal concentration of 2 mM AH_2QDS. The reactors were sealed and agitated quickly to ensure a homogenous mixture and then left to react for 48–72 h with occasional mixing by hand. Control systems consisted of a homogeneous reactor with U^{VI} and AH_2QDS but no clay mineral, a sorption reactor with U^{VI} and clay mineral but no AH_2QDS, and a precipitation reactor with U^{VI} but without clay mineral or AH_2QDS.

2.3. Aqueous uranium analysis

Aqueous uranium concentrations were measured by ICP-OES at the U emission line at 385.958 nm using a PerkinElmer 4300DV instrument; samples were spiked with 11.2 μM Y as an internal standard with Y emission intensity measured at 371.029 nm. U concentrations resulting from reactions with the solids were measured after centrifugation with a detection limit of approximately 0.25 μM after 2-15× dilution of the samples in 5% nitric acid. This detection limit results in an accuracy of 5% or better for the determined concentrations of >5 μM U and enables accounting for the partitioning of >99% of the added U between the solid and solution phase. Better detection limits and accounting for the aqueous components dissolved from the clay would be needed to comment on the solubility of the U phases formed in our system.

2.4. X-ray absorption spectroscopy

U L_{III} edge (17,166 eV) x-ray absorption spectroscopy measurements were carried out at the MR-CAT/EnviroCAT insertion device beamline

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